# SIMULATIONS OF SIMPLE NANOMACHINES IN CARBON NANOTUBE BUNDLES BASED ON CHIRALITY

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## ABSTRACT

Single-walled carbon nanotubes (CNTs) have been studied extensively since their discovery and identification by Iijima in 1993. Their impressive mechanical, electrical, and thermal properties have created new fields of study, and the benefits of this research are just beginning to be realized.

One potential use of CNTs is as a foundation for nanomachines. Another possible use, one that takes advantage of their mechanical properties, is the synthesis of high-strength, low-weight materials that could revolutionize infrastructure materials. A significant problem facing researchers for either of these applications is in finding techniques to engineer the load transfer between nanotubes. For applications in strong materials, maximizing the coupling between carbon nanotubes is important; for molecular machine applications, inducing relative motion and/or reducing friction between molecules is desired.

In the simulations reported herein, we examined seven periodic tube bundles arranged in a horizontal closest packing (HCP) array using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) molecular dynamics code. The forces required to move the center tube through the bundle were recorded using the LAMMPS program. Each chirality type and diameter produced a different force function as the van der Waals forces "rubbed" against each other.

One property discovered through the simulations is that certain chirality combinations produce useful behavior during the pullout process. One such behavior is the ultra-low frictional resistance experienced by certain bundles, which could improve efficiency within nano-oscillators. Another discovery is the rotation induced by extraction, both in center tubes and in the outer tubes, which could serve as the foundation for a nanogear system. The final behavior involves removing the freedom of rotation within the system, which greatly increases the magnitude of load transfer during extraction. These findings will be useful in future research in the areas of nanomachines and in advanced materials.

## 1. INTRODUCTION AND BACKGROUND

Carbon nanotubes (CNTs) are on the forefront of the science of nanotechnology. Although a few forms of multi-walled carbon nanotubes (MWCNT) were discovered independently as early as 1952 (see Radushkevich and Lukyanovich, 1952; Hillert and Lange, 1958; Baker et al., 1973; Endo, 1975), they did not gain worldwide attention until the rediscovery of MWCNTs by Iijima in 1991 (Iijima, 1991). Single-wall CNTs (SWCNT) were discovered 2 years later by Iijima and Ichihashi (1993) and Bethune et al. (1993). Since then, they have been widely studied for their remarkable mechanical, electrical, and thermal properties.

CNTs are believed to be the strongest molecule discovered to date because of the $sp^2$ carbon-carbon bond present within the tube. A CNT is essentially a form of graphite that has been rolled into a tube of some arbitrary length. Carbon atoms are arranged in a lattice that spreads the load evenly across all of the carbon bonds in a tube. When this property is coupled with highly controlled synthesis, for example, controlling the length and/or chirality of the CNTs, a world of exciting possibilities opens up.

Carbon nanotubes are composed of a hexagonal lattice of carbon atoms called graphene that has been rolled into a tube. The actual arrangement of how the graphene sheet is rolled into a tube is called its chirality. The consistent, repeatable lattice formation provides the favorable properties. The favorable mechanical properties of CNTs also take advantage of the strong $sp^2$ C-C bond found throughout the lattice. SWCNTs use a single layer of graphene to form the tube. MWCNTs use two or more sheets to form concentric tubes where the outer tube could

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be described as a sheath.

Complex nanomechanical systems are one goal of nanotechnology research. Nanomachines can be used to build new molecules, manipulate existing molecules at the molecular level, and destroy molecules if necessary. These services are useful since direct manipulation of a single molecule at the molecular level can be extremely difficult.

In this study, we examined all three chirality types at three sets of sizes. Only tubes of similar diameter were placed together in a bundle. All nanotube types were simulated as both homogeneous bundles of a single chirality as well as heterogeneous bundles where a single nanotube of one chirality was surrounded by six nanotubes of another chirality type.

A carbon nanotube is constructed from a rectangular segment cut from a graphene sheet rolled into a seamless tube. The chirality of a CNT represents the angle at which the graphene is rolled back on itself. Chirality determines the symmetrical form of the force fields of the CNT wall, which in turn determines the interaction of the CNTs within the bundle. There are three distinct forms of chirality: armchairs, zigzag, and chiral. From these forms, an infinite number of diameters could be formed. In Fig. 1, the vector *l* is equal to the length of the carbon nanotube and parallel to the axis of the carbon nanotube. The width of the segment is determined by the chiral vector, *C*(*n*,*m*), which also determines the chirality of the carbon nanotube.

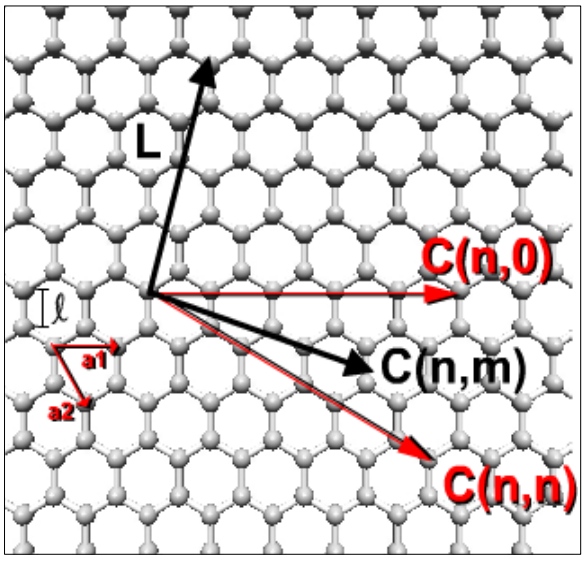


Fig. 1. An explanation of the chiral vector.

A carbon nanotube is completely described by its length and chirality. The chiral vector is a linear combination of the unit vectors that define the hexagonal lattice, α1 and $\alpha_2$, as shown in the equation below:

$$C(n,m) = \vec{n}a_1 + \vec{m}a_2$$

where *n* and *m* are integers and $n \geq m$.

The normal of the chiral vector is the circumference of the carbon nanotube. The diameter of a carbon nanotube can thus be written in terms of the C-C bond length *l* and the chiral vector indices *n* and *m* as follows:

$$D_{CNT} = \frac{\sqrt{3}}{\pi} l \sqrt{n^2 + mn + m^2}$$

As previously mentioned, the three different distinct types of chiralities are found in CNTs. Armchair tubes can be considered the standard type of CNT that is commonly the subject of simulations. The indices of this type of chirality are of the form (*n*, *n*). This chirality is symmetrical. Zigzag CNTs are also symmetrical except that the chirality vector is rotated 30 degrees. Nanotubes of this chirality have the form (*n*, *0*). A chiral nanotube is any other chirality with a chiral angle between those of armchairs and zigzags. These nanotubes have a staircase-like track of carbon hexagons along the length of the tube. The angle of the staircase is determined by the angle of the chiral vector. Fig. 2 shows the resulting CNT structure from each of these three types.

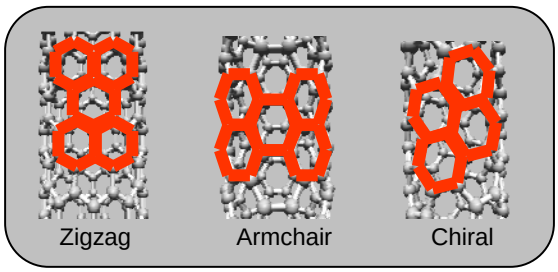


Fig. 2. The three types of CNT chirality.

Our research focuses on realizing the high-performance mechanical properties of CNTs in new novel construction materials. We performed our studies using tight-binding and molecular dynamics software since it gives us the power to investigate different molecular configurations that would not be easily recreated in a laboratory setting. For example, our previous studies predicted the maximum tensile strength and brittle failure of a (5, 5) chirality nanotube to be 15.5 million psi (Haskins et al., 2007). We were then able to take the same tube, copy it, and introduce a variety of different defects to the atomic structure. These different defects were then simulated to show how tensile strength was affected in comparison to the perfect original. We also discovered that a (10, 5) chiral CNT with a single atom vacancy in the lattice would create nonbrittle failure, and we also examined ways of inducing nonbrittle failure in our

original (5, 5) CNT (Majure et al., accepted for publication).

Our later research moved from single CNT systems to bundles of CNTs that interact with each other. More specifically, we examined CNTs in hexagonal closest packing (HCP) configuration. We found that CNT fibers bound only by van der Waals forces are not as strong as the constituent CNT because of the weak adhesion between CNTs. They simply slide past each other.

Others have examined CNT bundles, chirality, and simple nanomachines as well. A team at Berkeley led by Professor Zettl has developed rotational bearings from nested multiwall nanotubes by creating an electrostatic difference between the inner and outer tube (Cumings and Zettl, 2000). The work was done in situ in a scanning electron microscope (SEM). These nanoelectro-mechanical systems (NEMS) are the next step in miniaturization, which may find their way into commercial applications in the future.

Tangney et al. (2004) studied CNT oscillators in terms of frictional energy dissipation. Others have looked at friction between CNTs and graphene sheets (Buldum and Lu, 1999; Cheng and Lu, 2006). Still others have examined the effect of the diameter on the performance of a CNT bundle, but they did not specifically examine chirality. Their focus was the deformation of the tube as a result of bundle pressure (Jiang et al., 2008).

Our original purpose for examining these systems was to increase load transfer within a bundle by using interlocking chiralities and larger diameters. In this study, we examine how purposeful arrangement of CNTs of certain chiralities can create energy states favorable for nanomechanical machines. These machines may be useful in designing larger, more complex machines that could provide a useful function.

## 2. METHODOLOGY

For this study, we designed models that paired different combinations of chiralities for the outer six CNTs of the HCP configuration that are in contact with the inner CNT. An example of this configuration is shown in Fig. 3. We used quenched molecular dynamics simulations to investigate the effects of chirality on the van der Waals forces between HCP bundles of carbon nanotubes. We used the molecular mechanics software Large-scale Atomic Molecular Massively Parallel Simulator (LAMMPS) (Plimpton, 1995). LAMMPS has a Reactive Bond-Order Potential (REBO) (Stuart et al., 2000) for calculating potential energy between hydrocarbons. All CNTs are aligned along the z-axis, and all models are periodic along the z-axis.

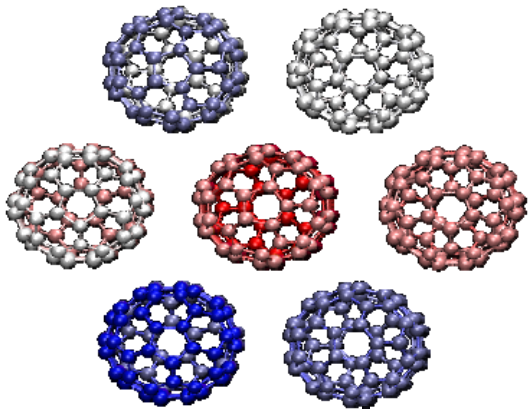

Fig. 3. An example of HCP configuration with nanotube oriented along the z-axis. Orthogonal visualization is used.

To perform quenched molecular dynamics, the model is initially quenched to the lowest possible energy state. This causes the van der Waals force to draw the CNTs together to their equilibrium point and adjust the orientation of the CNTs to allow the carbon electron shells to fit together at their lowest energy configuration. After equilibration, the center CNT of the HCP configuration is translated along the tube axis. The tubes are short enough that microstrains within the tube is not an issue (see Cornwell et al., submitted for publication). The entire tube is translated by adding 0.1 angstrom to the atom coordinates. After translation, the system is allowed to settle for a certain number of time-steps to allow any potential differences to be reconciled. After the system has settled, the next translation occurs and the process repeats. By repeating this process multiple times, the center CNT can be pulled infinitely and rubs against the six CNTs around it. The outer CNTs are fixed in place so that they are not allowed to be pulled along with the center CNT. They are held only in the z-direction so that the outer CNTs can move closer or farther from the center CNT if necessary and can rotate. An example of a CNT pullout test is shown in Fig. 4. No external outside pressure was applied.

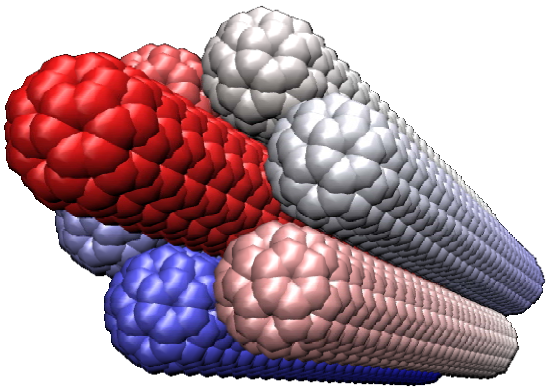

Fig. 4. An example of a non-periodic CNT pullout test similar to the periodic version performed.

We used LAMMPS to define groups of atoms and recorded the force required to pull the center CNT past the outer CNTs as well as the force required to hold the outer CNTs. These forces were compared to ensure that the system had equilibrated sufficiently. Since the system is periodic, the forces that are recorded are consequently periodic. The forces were compared to see which chiralities generate higher frictional forces than others. The original study discovered an interesting side effect. The process of pulling the center CNT past the outer CNTs created alignments along their respective chiralities and formed what are essentially corrugated surfaces between the two or more CNTs. These surfaces did more than create frictional force. We found that since graphene has a repetitive and consistent structure, predictable responses were produced that could eventually serve as piece of a larger nanomachine.

In this study, we examined all three chirality types at three sets of sizes. Only tubes of similar diameter were placed together in a bundle. All nanotube types were simulated as homogeneous bundles as well as heterogeneous bundles where a single nanotube was surrounded by six nanotubes of a different chirality type.

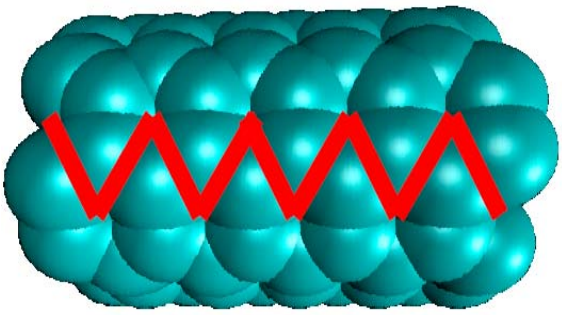

Fig. 5. Grooves created by van der Waals force fields on an armchair (5, 5) CNT.

An example of a normal pullout test simulated during this study considers a homogeneous (5, 5) CNT bundle. The (5, 5) CNT is an armchair and is highly symmetrical. During pullout from an HCP bundle, the center CNT and outer CNTs rotate slightly back and forth, matching the grooves created by the electron shells on the outside of a (5, 5) armchair as shown in Fig. 5. These grooves produce rotation because of the increase of potential energy when the shells slide past each other. The force calculated to perform this pullout is shown in Fig. 6. The rise and fall of this force function matches the frequency of the rocking motion seen in the CNTs. The forces are both assistive and resistive, and this is dependent upon the position of CNTs relative to each other. This simple example is representative of most of the other pullout tests that were performed between different chirality combinations.

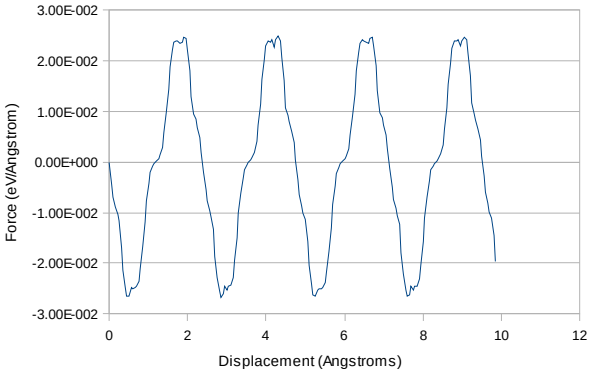


Fig. 6. Calculated pullout force of a single CNT from a homogeneous (5, 5) bundle.

## 3. ANALYSIS

We discovered three phenomena during our simulations. The first was the ultra-low friction created between armchair and zigzag CNTs. We examined a single (7, 7) armchair CNT surrounded by six (15, 0) zigzag CNTs and vice-versa. As mentioned earlier, both of these chiralities are symmetrical, with the main difference between the two being the orientation of the carbon hexagons found on the CNT wall. When the two types of CNTS are paired against each other, the perpendicular orientations create grooves that offset the opposing protrusions. The “hills” and “valleys” match up perfectly as they slide past each other. This pairing creates an ultra-low friction, and no rotation is necessary to relieve potential energy. The electron shells do not hinder the progress of the center CNT as it translates through the bundle. A graph of the force function for each of these simulations is shown in Fig. 7. Note that the peak forces are two orders of magnitude lower than the (5, 5) case mentioned earlier, and three orders lower in magnitude than the case of the homogeneous (15, 0) bundle.

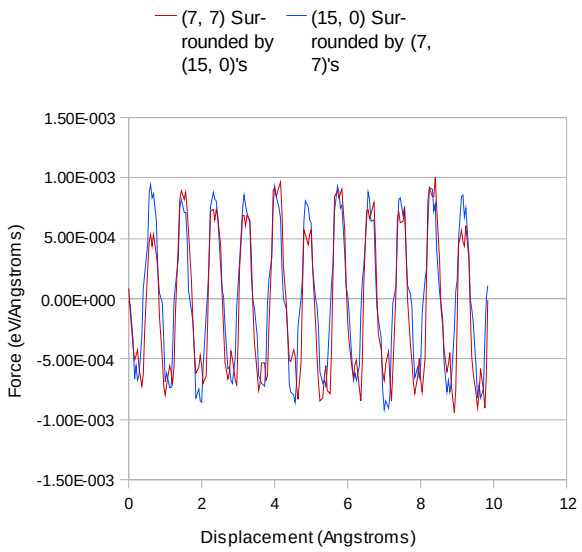


Fig. 7. Calculated pullout force of a (7, 7) CNT from a (15, 0) bundle and vice versa.

This finding could have important applications within nano-oscillators. Previous studies show that van der Waals forces create a capillary force for a single CNT protruding from a CNT bundle. This force will draw the CNT back into the bundle until it is protruding from the opposite side of the bundle. The van der Waals force then draws it back to the original position. This oscillation will continue as long as the CNT has enough momentum to carry it through the bundle and out the other side. Reducing any friction that occurs as the CNT passes through the bundle would be beneficial to the efficiency of the oscillator. This bundle configuration is much more efficient than any other chirality combination that was simulated.

The second result is the induction of rotation within CNT bundles completely on the basis of chirality. As stated earlier, chiral nanotubes have a staircase-like track of carbon hexagonal rings that encircles the length of the tube. The van der Waals force fields associated with these tracks create grooves that also encircle around and up the tube. We found that (10, 5) and (14, 7) CNTs seem to consistently induce rotation in the bundle. We observed three divisions of rotation: in-place rotation of the center CNT, synchronized in-place rotation of the outer six CNTs, or rotation of all six outer CNTs around the center CNT. This last type is analogous to a planetary motion gear system. Fig. 8 shows all three types of rotation possibilities that were observed. Rotation is caused by the alignment of the chiral-shaped van der Waals force fields. Models that did not contain a chiral nanotube did not make full rotations, although some did rock back and forth.

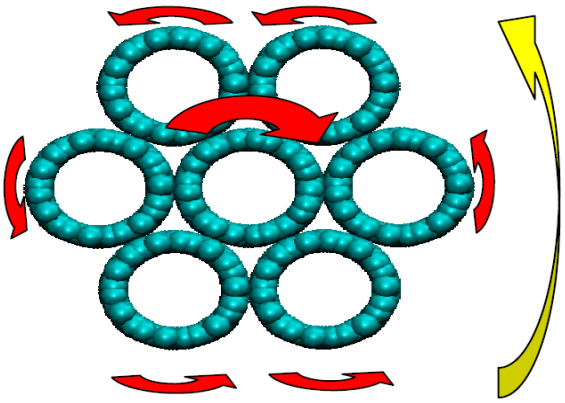

Fig. 8. The rotational styles seen in this study.

The model that best represents all three rotational styles is a (15, 0) zigzag nanotube surrounded by (10, 5) chiral CNTs. As the center CNT is translated in this simulation, it slowly rotates clockwise (CW). The outer six CNTs also rotate in place counterclockwise (CCW). Finally, the six outer CNTs rotate as a group CW around the center CNT. The diameter of the chiral nanotube determines the speed of the rotation, much as a normal gear system would. Changing the diameter and chirality of the tube could easily introduce gear ratios to control rotational speed.

The force required to extract the center CNT is also very different from those of the other models. While most of the other models created force functions that alternated between assisting and resisting the translation process, rotational systems effectively turn the center CNT into a threaded screw that has a consistently resistive force function. These functions consume more energy than the nonrotational system, which might be useful in creating a type of shock absorber. Previous studies have found that increasing pressure to the bundle increases frictional force between CNTs significantly. Adjusting the pressure could control the strength of the absorber. Fig. 9 compares this rotational system and the (5, 5) system originally discussed.

The final result is the increase in friction caused by restricting rotation. We found that HCP bundles that were not allowed to rotate experienced higher frictional forces than CNTs that were allowed to rotate. This finding makes sense, given the reason that the systems were rotating originally. Since the systems can no longer follow a minimum energy path, more energy is required to overcome the mismatched corrugated surfaces. Fig. 10 compares the restricted and nonrestricted versions of the (5, 5) homogeneous bundle and of the (15, 0) CNT surrounded by (10, 5) CNTs. This finding could be used as a braking system in a nanomachine. In the case of the rotating CNT gears, selective restriction of rotation to one

CNT might stop the rotation of a larger system.

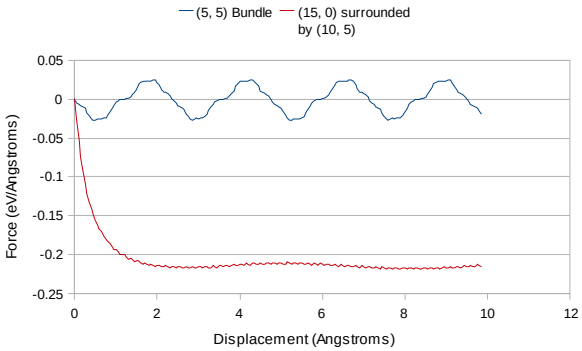


Fig. 9. A comparison of a rocking CNT pullout versus a fully rotating CNT pullout.

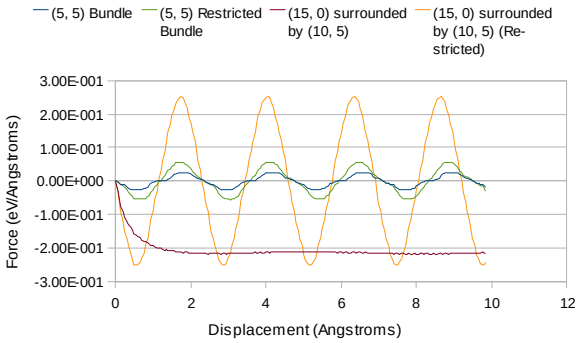


Fig. 10. Comparison of restricted and nonrestricted pullout forces.

## 4. CONCLUSIONS

This paper presents a few of the possibilities that exist for engineering CNT bundle properties based on chirality. These configurations have applications in nanomachine technologies by improving efficiency and enabling new design methodologies that were not available before. While synthesis techniques capable of creating these configurations have yet to be developed, we believe these designs will help create mechanisms that will power nanomachines in the future. Our findings can serve as a basis for nanomachines design of the future. Such nanomachines could assist the warfighter in areas such as energy harvesting, sensors, self-cleaning surfaces, or drug delivery systems, for example.

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